



Ion beam-induced luminescence and photoluminescence of 100 MeV Si⁸⁺ ion irradiated kyanite single crystals

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ABSTRACT

Ionoluminescence (IL) of kyanite single crystals during 100 MeV Si⁸⁺ ion irradiation has been studied in the fluence range $1.87\text{--}7.50 \times 10^{11}$ ions/cm². Photoluminescence (PL) of similar dimensional crystals was recorded with same ions and energy in the fluence range $1 \times 10^{11}\text{--}5 \times 10^{13}$ ions/cm² with an excitation of 442 nm He–Cd laser beam. A sharp IL and broad PL peaks at ~ 689 and 706 nm were recorded. This is attributed to luminescence centers activated by Fe²⁺ and Fe³⁺ ions. It is observed that up to a given fluence, the IL and PL peak intensities increase with increase of Si⁸⁺ ion fluence. The stability of the chemical species was studied on with and without irradiated samples by means of FT-IR spectroscopy. The results confirm that the O–Si–H type bonds covering on the surface of the sample. This layer might be acting as a protective layer and thereby reducing the number of non-radiative recombination centers.

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1. Introduction

Ion beam-induced luminescence (IBIL) or ionoluminescence (IL) is a powerful technique for materials analysis. An ion beam is used to excite atoms in a target, and visible light emitted from the target material is analyzed with a spectrometer. Since, the visible light is emitted from outer-shell transitions, IBIL can be used to get information about the nature of chemical bonds as well as defects and impurities present in ppm levels [1–5]. On the other hand, in the conventional ion beam analytical techniques such as Particle induced X-rays Emission (PIXE), Rutherford Backscattering Spectroscopy (RBS) and Nuclear reaction methods (NRA), it can measure only the elements without any information about chemical states. The photoluminescence (PL) spectroscopy is a contact less, non-destructive method of probing the electronic

structure of materials. It can be used to identify specific defects and their relative concentration and is able to identify those defects, which overlap in absorption [6]. Data on IL and PIXE of minerals [7–9], thin film [10] and semiconductor [11] materials have been reported in literature. However, a very limited work has been carried out on IL and PL of kyanite using ion beam irradiation [12].

Kyanite (Al₂SiO₅) is a natural single crystal, triclinic, occurs in long thin blade form, blue in color, semi-transparent. Iron is the major impurity along with traces of K, and Zn (in ppm level) in the crystal. Kyanite is used in the production of non-cast tank blocks, manufacture of spark plugs and as mineral specimens [13,14]. In the present paper, an attempt has been made to study the chemical states of elements in the sample and effect of ion irradiation due to 100 MeV Si⁸⁺ ions on kyanite single crystals using the techniques of IL and PL.

2. Experimental

The polished natural kyanite single crystals (~ 0.25 mm thickness and area ~ 25 mm²) procured from Indian Bureau of Mines, Bangalore are used in this experiment. The samples are

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cleaned using acetone and double distilled water and thereafter used for further studies. The samples were irradiated with 100 MeV Si^{8+} ions by using a 15UD Pelletron Accelerator at Nuclear Science Center, New Delhi, India. These studies were performed at room temperature (RT) in the experimental chamber and vacuum better than 10^{-7} Pa. The broad beam was scanned over a $5 \text{ mm} \times 5 \text{ mm}$ area on the sample using a magnetic scanner with beam current 2 pA. The dose accumulated in the sample was measured separately in terms of fluences and the following fluences were used $1.87\text{--}7.50 \times 10^{11} \text{ ions/cm}^2$ (IL) and $1 \times 10^{11}\text{--}5 \times 10^{13} \text{ ions/cm}^2$ (PL). The detailed IL set up was described elsewhere [15]. The PL emission spectra of pristine and ion irradiated samples were recorded using He–Cd laser (KIMMON) and a Mechelle 900 spectrograph working in the 200–1100 nm wavelength region. It has a cooled CCD array based detection system. The laser light is incident on the sample at 45° and the luminescence light is collected using a collector assembly and transmitted to the spectrograph through an optical fiber for detection and analysis. The spectral calibration was done using a mercury pen lamp. The linear spectral resolution in the present configuration was 0.5 nm. The FT-IR measurements were carried out using Bio-Rad instrument. The elemental analysis is performed by Energy Dispersive Spectroscopy (EDS).

3. Results and discussion

IL spectra of kyanite single crystals acquired during 100 MeV Si^{8+} ions irradiation in the fluence range $1.87\text{--}7.50 \times 10^{11} \text{ ions/cm}^2$ are shown in Fig. 1. A pair of sharp IL peaks at 689 and 706 nm is recorded after subtracting the background noise. The IL intensity at the peaks of 689 and 706 nm as a function of Si^{8+} ion fluence was studied and shown in Fig. 2. At the beginning of the ion irradiation the IL intensity increases rapidly, stabilizes and remains constant for higher fluences. The rapid increase in IL intensity is caused due to increasing number of intrinsic defects produced by ion irradiation. The sharp peaks recorded at 689 and 706 nm are attributed to luminescence centers activated by Fe^{2+} and Fe^{3+} ions [16]. These results are in good agreement with those reported in the literature [17,18]. Preliminary elemental analysis of the kyanite by EDAX reveals the presence of 52.65 at.% Al, 45.67 at.% Si and 1.67 at.% Fe as major impurities. The characteristics of the center giving rise to sharp emission in kyanite might be due to the fact that optically active electron involved in the luminescence emission is within 3d shell which is partially shielded by the outermost electrons $3s^2 3p^6$ [19].

The full width at half maximum (FWHM) of 689 and 706 nm peaks was calculated after base line correction and found to be $\sim 5 \text{ nm}$. The interval for the two chemical states of Fe^{2+} and Fe^{3+} ions was calculated and found to be 16 nm. Usually the FWHM of the peaks is less than the interval for two chemical states; it is good enough to analyze the oxidation states of the elements as an impurity in crystals or in some geological samples [17]. However, Sha et al. [17] have studied the IL of aluminum silicate (feldspar) bombarding with 2.4 MeV proton beam. They reported two peaks at ~ 2.241 and 1.817 eV corresponds to Fe^{2+} and Fe^{3+} ions and the interval between the two peaks is 129 nm. Homman [18] has studied the IL of plagioclase feldspar and reported the IL emission at 710–750 nm is due to Fe^{3+} ions in the Al^{3+} site. A similar geological sample of plagioclase feldspar was analyzed [6] using IL, the authors have observed a single Fe^{3+} peak. This could be due to the sample origin. Even though the sample is same, the impurities may vary from place to place. Brooks et al. [10] have studied the IL of feldspars irradiated with 3 MeV H^+ and He^+ ions. They observed that IL intensity decreases with increase of ion fluence. This decrease in IL intensity is attributed to variation in the Fe–O bond distances.

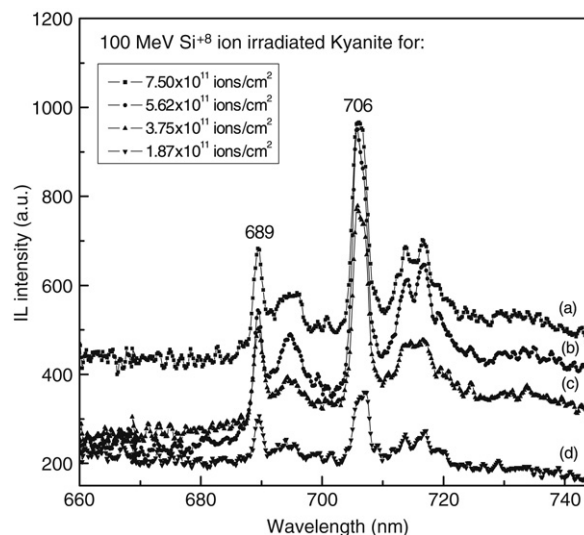


Fig. 1. Ionoluminescence spectra of kyanite crystals irradiated with 100 MeV Si^{8+} ions for (d) $1.87 \times 10^{11} \text{ ions/cm}^2$ (c) $3.75 \times 10^{11} \text{ ions/cm}^2$ (b) $5.62 \times 10^{11} \text{ ions/cm}^2$ (a) $7.50 \times 10^{11} \text{ ions/cm}^2$.

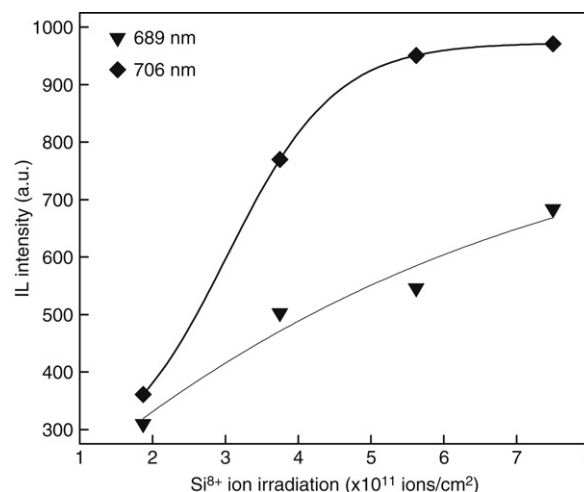


Fig. 2. Variation of IL intensity at 689 and 706 nm peaks as a function of Si^{8+} ion fluence in kyanite crystals.

Skuratov et al. [20] have reported the R-line luminescence spectra in ruby with 710 MeV Bi^+ ions with a fluence of $10^{12} \text{ ions/cm}^2$. The decrease in IL intensity with increase of ion fluence is due to stress effect. Wang et al. [21] have studied the amorphization of kyanite bombarded with 1.5 MeV Xe^+ ions with fluence of $1.88 \times 10^{14} \text{ ions/cm}^2$ using selected area diffraction pattern. Amorphization in the sample as each incident ion may create one or more several displacement cascades, which become amorphous as a result of rapid quenching, and then cascades eventually overlap to form an amorphization of solid. In the present studies, amorphization was not achieved. Because, it requires some more fluence to study the amorphization.

Fig. 3 shows the PL spectra of kyanite single crystals after bombarded with 100 MeV Si^{8+} ions in the fluence range $1 \times 10^{11}\text{--}5 \times 10^{13} \text{ ions/cm}^2$ with an excitation of 442 nm He–Cd laser beam. A pair of broad PL emission peaks at 689 and 706 nm was recorded in the entire samples. The peak positions are identical to those analyzed by IL method. The variation of PL intensity at 689 and 706 nm as a function of Si^{8+} ion fluence was studied and it is interesting to note that PL intensity increase significantly with increase of ion fluence and saturates for higher fluences (Fig. 4). The increase in PL intensity is attributed to creation of new traps with

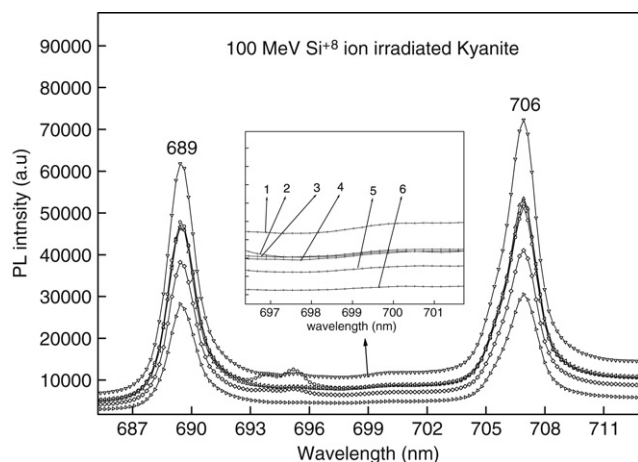


Fig. 3. Photoluminescence spectra of 100 MeV Si^{8+} ion irradiated kyanite crystals at different fluences (1) 1×10^{13} ions/cm² (2) 5×10^{12} ions/cm² (3) 1×10^{12} ions/cm² (4) 5×10^{11} ions/cm² (5) 1×10^{11} ions/cm² and (6) pristine.

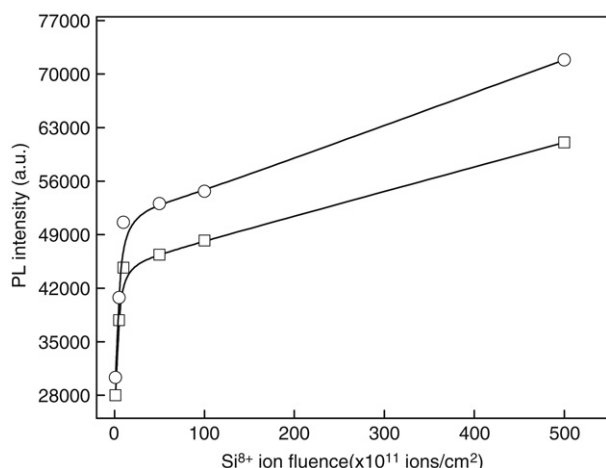


Fig. 4. Variation of PL intensity at 689 and 706 nm peaks as a function of Si^{8+} ion fluence in kyanite crystals.

the ion bombardment. With higher fluences, PL intensity is dose independent as a result no more ions could be accepted. Therefore it shows saturation.

The stability of the chemical species was studied by means of Fourier transformed infrared Spectroscopy (FT-IR) spectra using 100 MeV Si^{8+} ions in the fluence range 1×10^{11} – 5×10^{13} ions/cm² in the range 400–4000 cm^{-1} . Fig. 5 shows FT-IR spectra of Pristine (Un-irradiated) and 5×10^{13} ions/cm² irradiated samples. However, even though we have studied all the fluences, because of overlapping of curves/modes at below 1000 cm^{-1} , we have shown in figure only Pristine and 5×10^{13} ions/cm² irradiated samples. The assignment of infrared absorption peaks are presented in Table 1. It is interesting to note that, in addition to Si–O, Si–O–Al and Al–O bonds that exists in the un-irradiated kyanite, a new absorption peak has appeared in the irradiated kyanite sample at 2250 cm^{-1} . This peak corresponds to O–Si–H bond. This O–Si–H and –OH type bonds covering the surface of the sample and providing a protective and passivating effect as a result the number of non-radiative recombination centers can be reduced thereby increasing the intensity of IL and PL [22].

The irradiation effects may lead to the restructuring of the surface chemical species because of the energy deposited through electronic energy loss during the process of swift heavy ion irradiation and formation of ion induced defects leading to non-radiative recombination centers. These two processes are

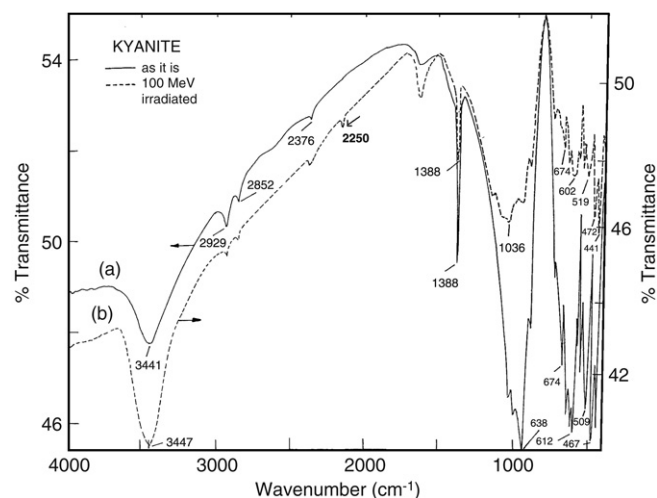


Fig. 5. Fourier Transform Infrared spectra of (a) pristine and (b) Si^{8+} ion irradiated (5×10^{13} ions/cm²) kyanite at room temperature.

Table 1

Assignment of band positions of Fourier transform infrared spectra of pristine and Si^{8+} ion irradiated kyanite

Absorption peak (cm^{-1})	Pristine sample	Irradiated sample
467–472	Si–O (ν_4)	Si–O (ν_4)
566–571	Si–O–Al	Si–O–Al
747–829	Al–O	Al–O
1109–1114	Si–O (ν_3)	Si–O (ν_3)
1160	Si–O (ν_2)	Si–O (ν_2)
2250	–	O–Si–H
2376–2929	Si–O ($2\nu_3$)	Si–O ($2\nu_3$)
3441–3461	–OH (ν_1, ν_3)	–OH (ν_1, ν_3)

simultaneous consequences of irradiation and they compete with each other. The enhancement in the IL and PL intensity might be due to balance between these two effects. Even though IL is a very sensitive technique, it is difficult to analyze natural/synthetic minerals quantitatively. The reason is that, the luminescence effects such as activation, co-activation and sensitization process can complicate the linearity between the IL, transition-metals and rare-earth ions present in the sample. A detailed study for quantifying those effects may be needed before the IL can be utilized quantitatively. PIXE can be great tool to relate those luminescence effects to the ions content quantitatively. Further experiments are in progress for obtaining a better understanding of these aspects.

4. Conclusions

The IL is a convenient and more appropriate technique to identify the type of impurity, oxidation state in geological/synthetic minerals and other types of materials. The sharp IL and broad PL peaks at 689 and 706 nm is attributed to luminescence centers activated by Fe^{2+} and Fe^{3+} ions, respectively. The increase in IL and PL peak intensities with Si^{8+} ion fluence might be attributed to O–Si–H type species covering the surface of the sample. This layer might be acting as a protective layer and thereby reducing the number of non-radiative recombination centers.

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